Short communication

In-situ observation of one silicon particle during the first charging

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HIGHLIGHTS

- Single particle measurement was performed for silicon secondary particle.
- The volume expansion behavior of silicon particles was in-situ observed successfully.
- The apparent volume expansion ratio of silicon was larger than the theoretical expectation.

GRAPHICAL ABSTRACT
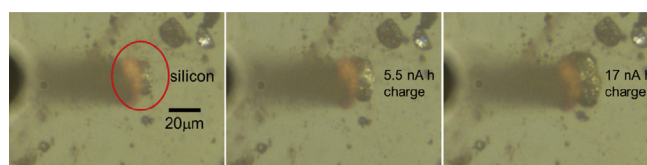
ABSTRACT

The understanding of volume change mechanism of silicon electrode is necessary to design a new negative electrode using silicon-based active materials. Here, the drastic volume expansion of one silicon secondary particle with μm-size was in-situ observed in order to find apparent volume expansion ratio during the first charging by using single particle measurement technique. The apparent volume expansion accompanied with the first lithiation is much larger than theoretical expectation due to the agglutination state and anisotropic property. The importance of direct observation with the single particle measurement has been affirmed for understanding the characteristics of silicon electrodes.

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1. Introduction

Lithium-ion batteries (LIBs) with high gravimetric and volumetric energy density are very important key devices to encourage popularization of an environmental friendly energy system which is consisted of solar cells, wind power generations, smart grid, and batteries. In addition, the batteries are extensively expected for a power supply of plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs). Further improvements in the energy density are major issues in order to increase the mileage per

charge [1]. New negative electrode materials with high capacity are of great concern, for example, tin based materials [2–4], lithium metal [5,6] and silicon based materials [7–26]. Compared with current negative electrode material, graphite (840 mA h cm^{-3}), the theoretical specific capacity of these materials is much larger; tin (1520 mA h cm^{-3}), lithium metal (1980 mA h cm^{-3}) and silicon (2440 mA h cm^{-3}). The energy density per volume not weight is very important because the standards of LIBs have been set for mobile phones, PHVs, and EVs. These materials alloying with lithium shows volume change more or less during charging (lithiation) and discharging (delithiation). The theoretical volume expansion of silicon electrode reaches by up to 400% during charging [7]. In other hands, discharging causes contraction of the lithiated silicon. The repeats of the volume expansion and

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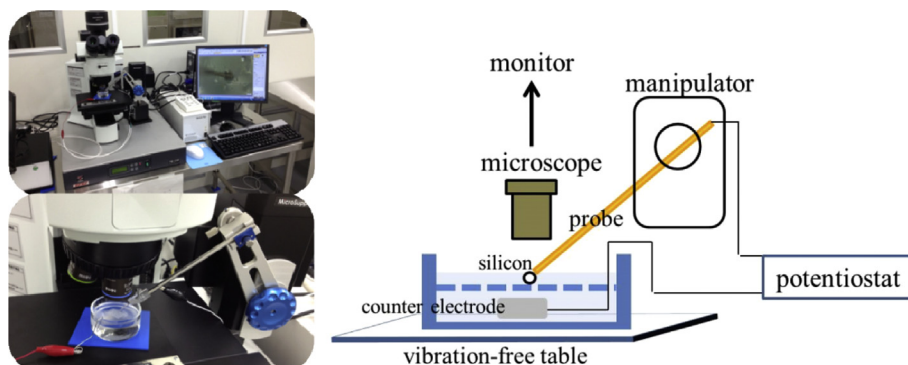E-mail address: NISHIKAWA.Kei@nims.go.jp (K. Nishikawa).

Fig. 1. A photograph (left) and a schematic diagram (right) of a single particle measurement system in the dry room. The probe of micro electrode was controlled by a micromanipulator to contact the probe with a silicon particle.

contraction induce an electrode failure due to the occurrence of cracking in the active materials and the electrical disconnection with a current collector. Numerous investigations have focused on how to restrict or avoid the volume change of silicon based active materials during cycles [7–26]. The improvements of the electrical connection during charging and discharging have been reported by using a new binder [12]. Liu et al. reported that new polyfluorene (PF)-type polymer binders could accommodate the volume change of silicon to achieve good stability and cyclability. The other researches have focused to reduce the material size to nanometer range [13–22]. The nano-sized silicon electrodes show better electrode performance because the strain in silicon nanostructure is allowed by using surrounding free space. Lee et al. discussed the anisotropic volume change behavior of silicon nanopillars by scanning electron microscope (SEM) observation [15]. Liu et al. reported in-situ transmission electron microscope (TEM) observation of silicon nanowires (NWs) and nanoparticles during the lithiation, and the anisotropic volume change behavior [16,17]. These in-situ TEM researches have revealed anisotropic property of the lithiation of silicon electrode and a size dependence of cracking in the nano-sized silicon particle during the lithiation. Some researchers have compared theoretical studies with those researches for the lithiation mechanism of silicon electrodes [20,21]. Dahn et al. have researched the volume change of amorphous silicon and silicon-tin alloy thin film electrodes during charging and discharging by using in-situ atomic force microscopy technique [23,24]. Such in-situ measurement techniques help to understand the volume change mechanism. Although thin film electrode is very popular electrochemical model system to examine some basic properties and is applicable for some in-situ measurements, actual electrodes in current LIBs are composed of the powder active materials with μm size, conductive agents and binders. It is very important to reveal the electrochemical characteristics and the volume change behavior of not only primary nm-size silicon particles but also the agglutinated secondary particles with μm range in the liquid electrolyte as well as practical battery system. In this study, we introduce, for the first time, in-situ observation for the volume expansion behavior of a μm-sized silicon secondary particle during the first lithiation by a single particle measurement technique.

The single particle measurement system is a very powerful equipment to evaluate the electrochemical characteristics of active materials themselves in the practical battery electrolyte. Nishizawa and Uchida demonstrated the micro electrode system for the characterization of battery materials [27]. They utilized the system to investigate some positive electrode materials for LIBs [28,29]. The previous works of our group have revealed excellent electrochemical properties of LiCoO$_2$, graphite and LiFePO$_4$ single particle [30–32]. In this study, the single particle measurement system described schematically in Fig. 1 was located in a dry room. The dew point of the dry room was under 223 K with human, and under 203 K without human. Thus, the moisture contamination was ignorable during the electrochemical measurement. Compared with the conventional single particle measurement system located in a globe box filled in purified Ar gas, the system in the dry room has much better operation performance.

2. Experimental

A Pt microwire with 20 μm diameter was sealed in glass capillary [31]. The tip of the glass-sealed Pt microwire was cut to yield a microdisk, and then polished carefully to a mirror face. Cu was electrodeposited onto the Pt microdisk tip, because of the prevention for the electrochemical reaction of Pt with Li$^+$ ion during the
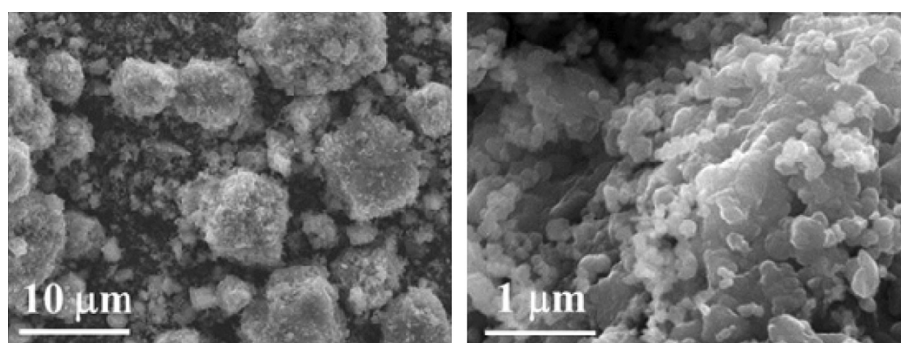

Fig. 2. SEM images of silicon particles at different magnification. Primary silicon particles size is about 100 nm, and these particles agglutinate to secondary particles with about from 5 μm to 20 μm diameter.
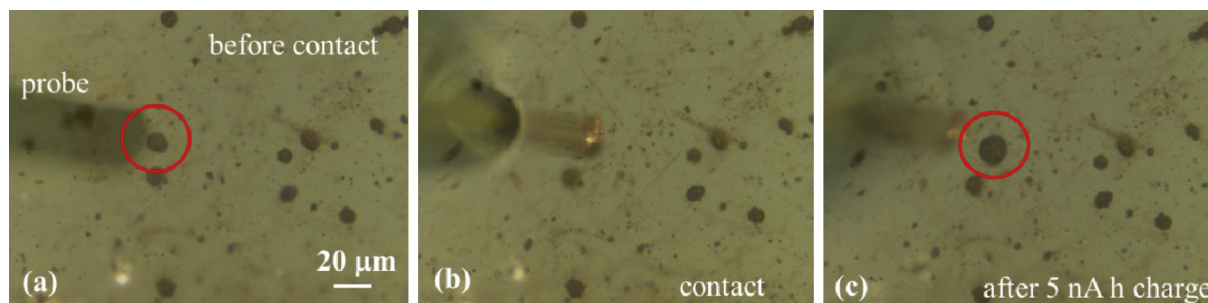
Fig. 3. Optical microscope images during single particle measurement of silicon. (a), before contact to silicon particle. (b), just after contact to the particle. (c), after 5 nAh charging (5 nA for 1 h). The electrolyte was 1.0 mol dm^{-3} in propylene carbonate/ethylene carbonate (1:1 by volume).

lithiation of a silicon particle. The Cu electrodeposition was carried out at a constant current condition of 31.4 nA for 30 min in 0.6 M $CuSO_4 \cdot 5H_2O$ and 5×10^{-4} M H_2SO_4 aqueous solution. The silicon powders (crystalline/amorphous, 99.9985%, Alfa Aesar) were dispersed on a glass-fiber sheet. The sheet was placed on the glass flitter in the electrochemical cell as shown in Fig. 1. The Cu electrodeposited micro electrode was attached to a silicon particle by using a micromanipulator (QP-2RH, Microsupport) under optical microscope (BX-51, Olympus) observation. And then, the electrochemical measurement was conducted. The electrolyte was 1 M lithium perchlorate in a mixture of propylene carbonate/ethylene carbonate (PC/EC, 1:1 by volume), from Kishida Chemical Co., Ltd.. The counter electrode was a Li foil supplied from Honjo Metal Co., Ltd. and the electrochemical measurements were performed with a two-electrode system. The galvanostatic charging (lithiation) tests were carried out with an electrochemical analyzer (ALS600D, BAS Inc.) up to 0.01 V vs. Li/Li$^+$. The temperature was kept 295 K in the dry room.

3. Results and discussion

SEM images of the silicon particles used in this study are shown in Fig. 2. The primary silicon particle size is about 100 nm, and these particles agglutinate to secondary particles with about from 5 μm to 20 μm diameter. The particle size is adequate to be attached by a micro electrode in the single particle measurement system. The

contact of the micro electrode with one silicon particle was performed by using the micromanipulator, as shown in Fig. 3. Fig. 3(a) shows one silicon particle before the contact with the micro electrode, and Fig. 3(b) shows the attachment of the micro electrode with the silicon particle. The micro electrode tip onto which the electrodeposition of copper was done is coppery brown. Fig. 3(c) shows the lithiated silicon with 5 nA h (5 nA, 1 h). It is very clear that silicon particle expanded during the charging, comparing Fig. 3(a) with Fig. 3(c). Thus, the single particle measurement technique can not only measure the electrochemical characteristics but also observe the volume change behavior of single silicon particle.

Fig. 4 shows a charge curve with 5 nA charging and the corresponding volume expansion behavior of another silicon particle. Fig. 4(a) represents the time transition of electrode potential of the silicon particle during 5 nA charging corresponding to 0.43 C-rate. The theoretical capacity was estimated from the silicon particle volume. After the charging starts, the potential drops quickly and shows a voltage plateau corresponding to a two phase region in which amorphous lithiated silicon is formed [25,26]. And then, the potential decreases gradually to reach the cut-off potential; 0.01 V vs. Li$^+$/Li. According to Li and Dahn [26], the amorphous lithiated silicon phase is transformed new $Li_{15}Si_4$ phase at that region (around 60 mV). Fig. 4(b) and (c) shows microscopic images before and after the charging, respectively. These images demonstrate
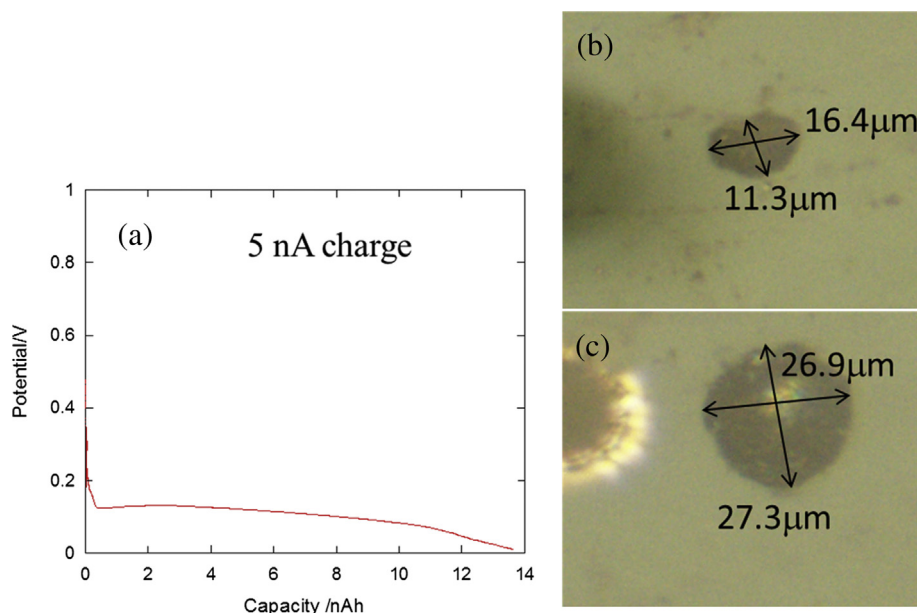

Fig. 4. Charge behavior of silicon single particle at 5 nA. (a), Charge curve of the silicon particle. (b), Optical microscopic image before the charging. (c), After charging of 13.5 nAh. The charge was conducted to 0.01 V vs. Li/Li$^+$.

very significant volume expansion of the silicon particle during the charging. In order to examine the volume expansion ratio of silicon particles, the particle volume was calculated on the basis of very simple hypothesis that the particle is sphere shape with average diameter; the average diameter in Fig. 4(b) is about 13.8 μm, therefore the volume is estimated to 1.39×10^{-9} cm^3. The averaged diameter of the lithiated silicon is about 27.1 μm. The volume is 1.05×10^{-8} cm^3 which is 7.6 times larger than before charging. One silicon atom can alloy with maximum 4.4 lithium atoms to form $Li_{22}Si_5$ phase, and then, it is known that 400% volume expansion occurs. However, in room temperature, $Li_{15}Si_4$ is the highest lithiated phase accompanied with 280% volume expansion [25,26]. This significant difference between the experimental result and the theoretical values may be caused by the following reasons. In this measurement, the silicon particles are secondary particles. This apparent expansion ratio should include the interspaces between the primary silicon particles. The primary silicon particles may show smaller volume expansion. However, the active materials are often agglutinated to μm-size in the composite electrode of the practical batteries. It is indispensable to find the volume change behavior of the secondary particles with μm-size as well as the primary particle with nm-size. Furthermore, some researchers have found that the volume expansion behavior of crystalline silicon particle shows anisotropic property. The volume expansion along the <110>direction is preferential because the interfacial energy for the (110) interface is the smallest [15–17,20,21]. Although it is difficult to discuss the crystal orientation dependence of volume expansion in the single particle measurement system, the large apparent volume expansion may be affected by such anisotropy. These are reasons why the apparent volume expansion ratio is much larger than theoretical expectation.

The apparent expansion ratio of silicon particle diameter with respect to the charging capacity per the silicon particle volume is demonstrated in Fig. 5. The applied current densities are between 0.1 and 0.5 C-rate. The blue and red lines (in the web version) represent the theoretical lines based on the assumption that the expansion will occur proportionally with Li content for $Li_{22}Si_5$ phase and $Li_{15}Si_4$ phase, respectively. Full lithiation phases of $Li_{15}Si_4$ and $Li_{22}Si_5$ correspond to 0.0083 and 0.0098 of x-axis values, respectively. The filled plots represent the fully lithiation and the open plots are not fully lithiated silicon particles because the micro electrode attachment sometimes was slipped due to the expansion of silicon particle during the charging. The full lithiation is
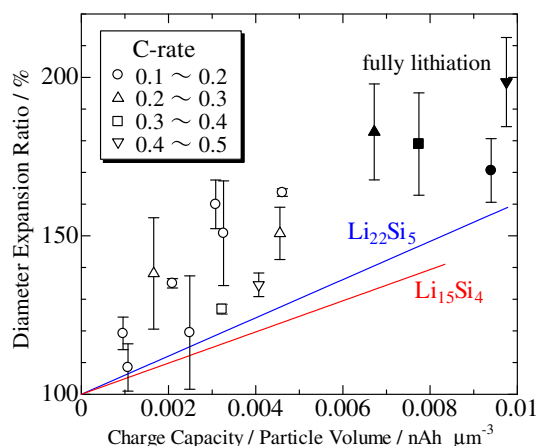
Fig. 6. The comparison of volumetric capacity of silicon (theoretical), silicon (in this study), graphite and Li metal.

estimated from the charging curve, which the electrode potential reached the cut off voltage smoothly, as shown in Fig. 4(a). Although not clear current density dependence of apparent volume expansion was observed in this current density region, it is very noticeable that all experiment results show larger volume expansion than the theoretical expectation. In order to design the new electrodes containing silicon-based materials, it is indispensable to understand the mechanism of not only the volume expansion during the lithiation but also the volume shrinkage during the delithiation. This is very challenging future work because it is difficult to keep the contact between the micro electrode with silicon particles while the contraction of lithiated silicon is proceeding due to the delithiation.

Finally, a comparison of the volumetric capacity of silicon electrodes with graphite and lithium metal electrodes is shown in Fig. 6. The first column represents the volumetric capacity of fully lithiated silicon with theoretical 400% volume expansion, second column represents the volumetric capacity of fully lithiated silicon calculated based on the results shown in Fig. 4. Third and fourth columns show that of graphite and lithium metal, respectively. The fully lithiated silicon particle used in this study has at most 50% larger volumetric capacity than graphite electrodes, although theoretical capacity of silicon electrodes is three times larger than graphite electrodes. If the silicon based materials show smaller volumetric capacity than theoretically expectation value, as demonstrated in this study, we have to reconsider what materials is the most attractive for the negative electrodes. Perhaps, lithium metal will also become a competitive electrode candidate for the next generation batteries although the material has very complicated dendrites problems.

4. Conclusion

We showed that in-situ observation of silicon volume expansion accompanied with the first charging by the single particle measurement technique. The apparent volume expansion of one silicon secondary particle is larger than theoretical expectation, because the silicon particles used in this study were agglutinated by the primary particles with 100 nm size and the lithiation have anisotropic property. Such very large volume expansion may induce smaller volumetric capacity of silicon-based electrode materials. It is very important to find the actual precise volume expansion ratio of these materials for designing a new negative electrode, because the commercial LIBs for mobile phones, PHEVs and EVs are strictly defined by the battery cell volume nowadays. For the direct

Fig. 5. Expansion ratio of the diameter of lithiated silicon particle with charge capacity per the particle volume of before lithiation. The imposed current was varied from 1 nA to 5 nA. These values are corresponding to between 0.1 and 0.5 C-rate. The filled plots represent the fully lithiated silicon, and the open plots represent the partially lithiated silicon.
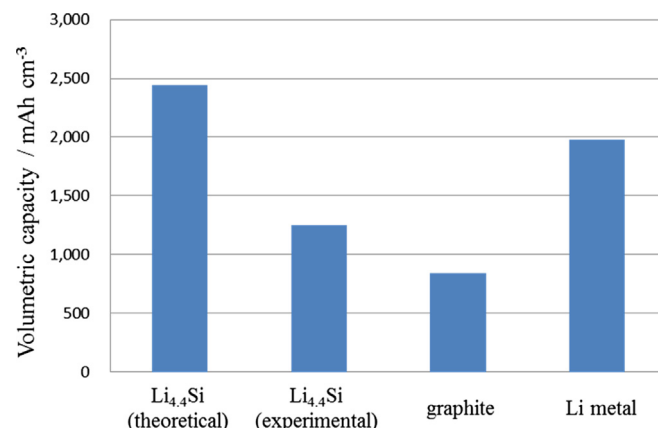
measurement of volume change behavior of silicon particles in practical electrolytes, it was affirmed that the single particle measurement system is very powerful technique.

Acknowledgments

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